

## Fabrication of Planar-Type Ti/TiO<sub>x</sub>/Ti Junction by SPM Local Oxidation for a Resistive Switching Device

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Metal/Insulator/Metal (MIM) junctions are promising to be a resistive switching device for a nonvolatile memory (NVM). It has been shown to offer the advantages of low power consumption, high speed operation, and high density integration. In general, MIM structures are fabricated by growing metal and insulating films into the stack layers (bottom-up approach). In this work, we demonstrate the planar-type MIM junction using a novel nanofabrication, known as Scanning Probe Microscopy (SPM). Planar-type Ti/TiO<sub>x</sub>/Ti junctions were fabricated on SiO<sub>2</sub>/Si wafer by sputtering of Ti thin films, and following with the local oxidation on Ti film by SPM. The growth of TiO<sub>x</sub> was investigated for morphological property by atomic force microscopy (AFM). The morphology shows that the insulating channel width are in order of 50-200 nm corresponding with the applied tip bias (-1 to -10 V) and the scanning rate (1 to 0.1 μm/sec). We introduce the growth mechanism to explain the TiO<sub>x</sub> formation based on the model of Huang.

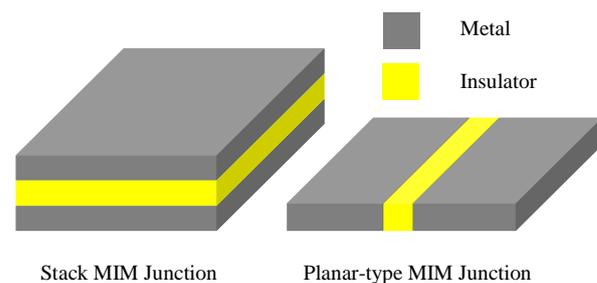
**Keywords:** Resistive switching, scanning probe microscopy, and local oxidation.

### 1. INTRODUCTION

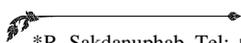
Resistive random access memory (RRAM) is one of the most promising next generation nonvolatile memories (NVM) [1]. RRAM has attracted research attention due to the advantages of low power consumption, high speed operation, and excellent scalability. The simple structure of resistive switching device consists of metal insulator metal (MIM) junction. The device changes the resistance under the applied electrical voltage or current. Thus the bias-voltage is used to control states of low resistance (SET) and high resistance (RESET). Recently, researchers are extensively focused to explain the resistive switching characteristics of many insulating materials with high-k dielectric such as ZrO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and HfO<sub>x</sub> [2,3]. Various mechanisms have proposed such as the formation/rupture of conductive filament in metal oxide layer and the interface barrier model of difference electrodes [1]. However, the origin of switching mechanism is not fully understood in RRAM research.

Generally, MIM structures are fabricated by growing metal electrode and metal-oxide insulator into the stack layers (bottom-up approach). However, this structure is difficult to analyze the conducting path and interface phenomena because of the very thin insulator layer. Therefore, we introduce a planar-type MIM structure using a nanofabrication method called scanning probe microscopy for the growth of metal-oxide insulator. The different between stack-type and planar-type structures is shown in Fig. 1. Scanning Probe Microscopy (SPM) is a

well known technique in surface characterization i.e. scanning tunneling microscopy (STM), atomic force microscopy (AFM), and magnetic force microscopy (MFM). Owing to the development of SPM, local oxidation nanolithography by atomic force microscope is recently interested for metal-oxide nanofabrication. The local oxidation reaction performed by a biased tip of AFM on metal substrate, employ the formation of the metal-oxide. The mechanism of local oxidation process has been reported by Garcia et al. [5] due to the field-induced oxidation, that need larger local electric field than the critical electric field to dissolve the water molecules to H<sup>+</sup> and OH<sup>-</sup> ions (typical about 1 V/nm) in water bridge formed around the tip and the sample surface. Then, OH<sup>-</sup> ions are transported by electric field created applied bias to metal surface and form the metal-oxide structures. The reaction is performed in atomic scale in the sample surface. In this work, the planar-type Ti/TiO<sub>x</sub>/Ti junctions were demonstrated and studied the mechanism of TiO<sub>x</sub> formation by SPM technique.



**FIGURE 1.** Metal insulator metal junction: Stack-type and Planar-type structures



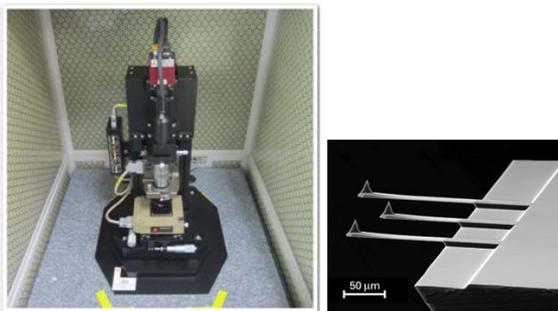
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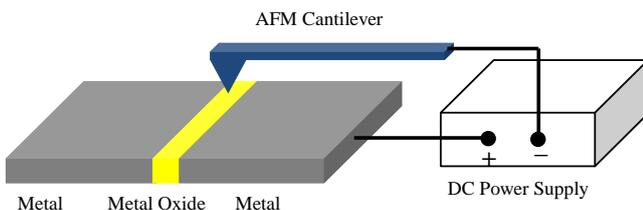
## 2. EXPERIMENT

Planar-type MIM junctions were fabricated on SiO<sub>2</sub>/Si(100) substrates. The substrates were cleaned using piranha solution (H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>, 3:1) for removing organic residue off substrates. Then, the substrates were rinsed with deionized (DI) water and ultrasonic cleaned for 15 minutes. Finally, the substrates were dried with compressed nitrogen gas and immediately loaded into the vacuum chamber. Titanium thin films were deposited by DC magnetron sputtering from 3 inch Ti target (purity 99.995%). The sputtering power was used at 80 W with the Ar gas pressure at 4.0x10<sup>-3</sup> mbar for one minute. The substrate bias was applied at 60V during the sputtering. With these parameters we have obtained the film thickness about 5 nm with a roughness of 0.15 nm.

A commercial AFM (Park systems model XE100) was used to perform local oxidation in contact mode AFM. A Si cantilever (NSC36 series, Mikromasch) having a diameter of approximately 200 nm with the angle <40° was perform the oxidation as shown in Fig.2. Local oxidation parameters were investigated on Ti surface by various conditions such as tip bias: -4V to -10V, tip scanning speed: 0.25µm/sec to 1 µm/sec and a constant applied force at 12.59 nN. Figure 3 illustrates the local oxidation on metal film by tip bias AFM. The humidity was control in standard acoustic enclosure about 60 %RH. Topological images of oxidized Ti surface were observed by contact mode AFM after the local oxidation. The parameter was optimized before used in the fabrication of the MIM junction. The planar MIM structure was designed with a dimension of 10x10 µm<sup>2</sup> using AFM software (XEL). The insulator has a rectangular size of 0.75x5 µm<sup>2</sup>. After the oxidation patterning, the as-grown samples were characterized the topology by AFM in non-contact mode.



**FIGURE 2.** AFM equipment for the growth metal-oxide and SEM image of the cantilever using in this work



**FIGURE 3.** Illustration of the local oxidation on metal film by tip bias AFM.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Local Oxidation Mechanism

Mechanism of local oxidation on Ti surface can be described in Fig. 4 which is modified from the model of GaAs oxidation proposed by Huang WP [6,7]. When an AFM probe is nearly to a Ti surface, the capillary force enhances a water bridge around the AFM tip and sample surface. AFM tip acts as a cathode while sample surface performs anode due to the polarity of the applied bias on electrodes. A high electric field dissociates the water into H<sup>+</sup>, OH<sup>-</sup> and charge ions. The formation of titanium oxide produces by electrochemical reaction as follows:

- Reactions at the Ti surface:  

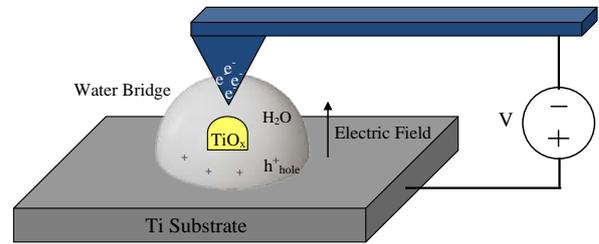
$$\text{Ti} + 2\text{H}_2\text{O} + 4h_{\text{hole}}^+ \rightarrow \text{TiO}_2 + 4\text{H}^+$$

$$2\text{H}_2\text{O} + 4h_{\text{hole}}^+ \rightarrow \text{O}_2 \uparrow + 4\text{H}^+$$
- Reaction at an AFM probe:  

$$4\text{H}_2\text{O} + 4e^- \rightarrow 2\text{H}_2 \uparrow + 4\text{OH}^-$$
- Reaction in water:  

$$4\text{H}^+ + 4\text{OH}^- \rightarrow 2\text{H}_2\text{O}$$

where, h<sup>+</sup><sub>hole</sub> is a positively charged hole on the Ti surface. In addition, H<sub>2</sub> and O<sub>2</sub> gases from the reaction expose to environment.



**FIGURE 4.** Schematic of local oxidation mechanism of TiO<sub>x</sub> on Ti Surface.

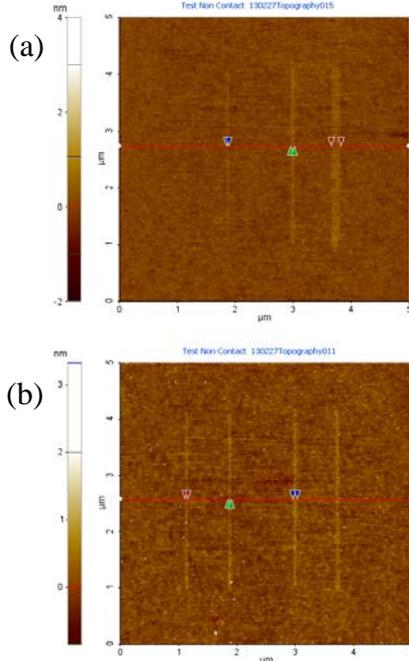
### 3.2 Topological information

AFM local oxidation results of Ti film as a function of the applied bias voltage and tip scan speed are presented in this section. A line pattern is used to perform the local oxidation on various test conditions. Fig. 5(a) shows the TiO<sub>x</sub> line pattern performed by tip scanning speed of 0.5 µm/sec and various tip bias -4, -6, -8, -10V from the left to the right hand side, respectively. The line width of TiO<sub>x</sub> is in the range of 40-170 nm with the increase of negative bias voltage. At bias voltage below -4 V, the oxide height cannot observe by AFM image. It may due to the low electric field and very low oxide formation. This result shows that bias voltage is very important for the oxide formation.

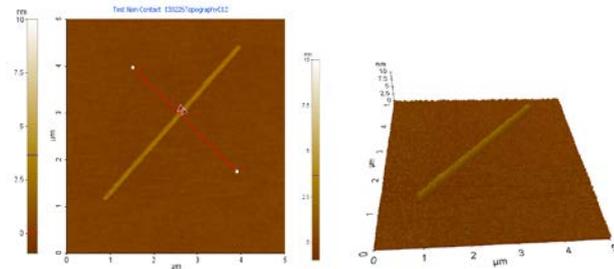
The scanning speed is an important parameter for performing oxidation time. Figure 5(b) presents TiO<sub>x</sub> line pattern performed by tip bias -8V and various tip scanning speed of 1, 0.75, 0.5, 0.25 µm/sec from the left to the right hand side, respectively. The line width of TiO<sub>x</sub> slightly increases in the range of 50-100 nm depending on decreasing of scanning speed. This result shows the saturation of oxidation reaction with scanning speed. Both parameters are optimized by considering the homogeneous of TiO<sub>x</sub> with the shortest time. Figure 6 shows the optimize

TiO<sub>x</sub> line performed by bias AFM tip bias -8V scan rate 0.5μm/sec. The line width and height are 120 nm and 2.5 nm, respectively.

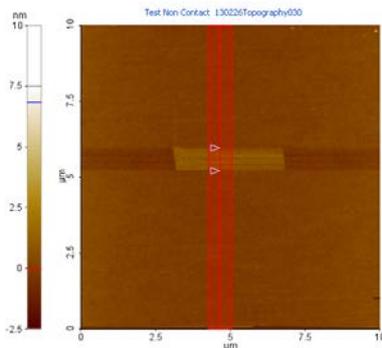
The optimized condition was used to fabricate TiO<sub>x</sub> insulating layer for MIM junction. The metal-oxide layer was designed with the dimension of 0.75 x 5 μm<sup>2</sup>.



**FIGURE 5.** (a) TiO<sub>x</sub> line pattern performed by tip scanning speed of 0.5 μm/sec and various tip bias -4, -6, -8, -10V (b) TiO<sub>x</sub> line pattern performed by tip bias of -8V and various tip scanning speed of 1, 0.75, 0.5, 0.25 μm/sec from the left to the right hand side, respectively.



**FIGURE 6.** Optimum TiO<sub>x</sub> line for fabrication of MIM junction (a pair of red cursor indicates the line width about 120 nm)



**FIGURE 7.** TiO<sub>x</sub> insulating rectangular pattern for MIM junction with a device dimension of 0.75 x 5 μm<sup>2</sup>

The fabrication time is about 30 minutes. Figure 7 shows the TiO<sub>x</sub> insulating rectangular pattern for MIM junction (bright color). The as-grown TiO<sub>x</sub> pattern is nearly the same with the designed pattern whereas the edge of rectangular is not perpendicular. A pair of red cursor indicates a rectangular width of 0.746 μm. We suggest that the problem may depend on the piezoelectric scanner of sample stage.

#### 4. CONCLUSION

In conclusion, planar-type MIM junctions were fabricated by SPM local oxidation on Ti thin film. The TiO<sub>x</sub> formation can be explained by electrochemical reaction of Ti with water bridge (H<sub>2</sub>O) based on the model of Huang. Both tip bias and tip scanning speed are important parameters in the fabrication. In this study, we found that the optimize condition is bias voltage of -8V and tip scanning speed of 0.5 μm/sec. The optimize condition were used to fabricate the MIM junction which shows the feasibility of fabrication planar-type Ti/TiO<sub>x</sub>/Ti junction for a resistive switching device.

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